

# Radius and surface tension of microscopic bubbles by second gradient theory

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## Abstract

The classical theory of Laplace is not suitable for describing the behavior of microscopic bubbles. The theory of second gradient fluids (which are able to exert shear stresses in equilibrium conditions) allows us to obtain a new expression for surface tension and radius of these bubbles in terms of functionals of the chemical potential. This relationship allows us to generalize the results of Cahn-Hilliard (1959) and Tolman (1948).

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## 1 Introduction

The microscopic bubbles we consider in this paper contain enough molecules to be modelled as a continuous strongly non-homogeneous system. To the clas-

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sical expression for the free energy valid for homogeneous continua has to be added a term depending on the variation of mass density. Usually the additional term is assumed to depend on the gradient of density only (Cahn, 1959; Serrin, 1986). Hence the expression for stress tensor differs from that valid for elastic fluids as even in equilibrium conditions shear components also appear. The form of the balance equation of force valid for second gradient fluids is found in Germain (1973), Casal (1962). In 1948, Tolman established, by using a Gibbs-like approach to Laplace theory, some relationships between the radius and the surface tension of bubbles in equilibrium with their liquid phase. This work produced many theoretical and experimental investigations concerning bubbles of quasi-molecular dimensions (Fisher, 1980; Kumar, 1991). In this case the theory of Laplace is not suitable as the vapour bubble consists mainly or exclusively of the interfacial phase. However, to interpret the experimental evidence it is still important to attribute a radius and an energy to microscopic germs: we do this by means of an *equivalent* model of Laplace type. We note that Cahn and Hilliard did not consider the mechanical aspect of the nucleation phenomenon. They only considered the thermodynamic pressure (*i.e.* the spherical part of stress tensor deriving from the classical expression for free energy) while in Casal (1985) is shown, for second gradient fluids, the existence of a capillary non-spherical stress tensor whose trace includes - but does not reduce to - quoted thermodynamic pressure. The analysis of some preliminary numerical calculations allows us to conclude that the theory of second gradient fluids, reinterpreted through a comparison with Laplace theory, leads to predictions closer to the experimental evidence than those available in the literature for radii close to the critical one. A further improvement is conceivable by considering non-constant capillarity coefficient as suggested by De Gennes (1981).

## 2 Equilibrium of bubbles and Gibbs rule by the second gradient theory

The balance equations of force for capillary fluids are available in the literature (*see e.g.* Serrin, 1986). The most simple model taking into account the non-homogeneity effects introduces a unique additional physical constant  $C$  (Casal & Gouin, 1985). Its value in mks units is very small: its effects are notable only inside interfaces. Balance of forces, in equilibrium conditions, reads ( $\tau, \rho, \Omega$  denoting stress tensor of non-dissipative capillary fluids, mass density and potential of body forces):

$$\operatorname{div} \tau - \rho \operatorname{grad} \Omega = 0, \quad (1)$$

with

$$\tau = -p \text{ Id} + C \text{ grad } \rho \otimes \text{ grad } \rho, \text{ where } p = \mathcal{P} - C \frac{(\text{grad } \rho)^2}{2} + C \rho \Delta \rho,$$

with denoting by  $\mathcal{P}$  and  $\Delta$  the thermodynamic pressure and the Laplace operator respectively. Equation (1) implies:

$$\text{grad } \mathcal{P} + \rho \text{ grad}(\Omega - C \Delta \rho) = 0. \quad (2)$$

With assuming isothermal equilibrium conditions, relation (2) becomes:

$$\mu(\rho) - C \Delta \rho + \Omega = C^{ste}, \quad (3)$$

where  $\mu$  is the specific free enthalpy (*i.e.* the chemical Gibbs potential) relative to the fluid in a homogeneous state with mass density  $\rho$  and temperature  $T$ . If  $\Omega$  is negligible, the equilibrium of a bubble surrounded by its liquid phase with density  $\rho_l$  is represented by a spherically symmetric profile of density satisfying (Rocard, 1952; Cahn & Hilliard, 1959):

$$C \frac{d^2 \rho}{dr^2} + 2 \frac{C}{r} \frac{d\rho}{dr} = \mu(\rho) - \mu(\rho_l). \quad (4)$$

Equation(4) has to be supplemented with appropriate boundary conditions:

- (a) because of spherical symmetry, the derivative of  $\rho$  vanishes at the origin,
- (b) as we have assumed that the bubble is surrounded by a homogeneous liquid, the derivative of  $\rho$  vanishes at infinity.

If  $\rho_l^P$  is the density of the liquid phase in the equilibrium state with plane interface and the function  $\mu$  is smooth enough, then the theory of Fuchs equations (Valiron) implies that:

(i) for every  $\rho_l$  in an interval  $]\rho_m, \rho_l^P[$ , Eq. (4) and conditions (a)-(b) uniquely determine an increasing mass density profile  $\rho(r)$  and in particular its value  $\rho_v$  at the origin: we say that  $\rho(r)$  satisfies the capillary fluids version of the *Gibbs Phase Rule*;

(ii) the function  $\rho$  is twice differentiable at the origin;

(iii) as  $\frac{d\mu}{d\rho} \rho_l > 0$ ,  $\rho$  converges at least exponentially to  $\rho_l$  when  $r$  tends to infinity. With denoting with a prime the radial derivative and by  $\psi$  the free energy per volume, Eq. (4) implies:

$$C \rho'' \rho' + \frac{2C}{r} \rho'^2 = \mu(\rho) \rho' - \mu(\rho_l) \rho', \quad (5)$$

and by integrating

$$\frac{C}{2}\rho'^2 + \int_0^r \frac{2C}{x}\rho'^2(x) dx = \psi(\rho) - \psi(\rho_v) + \mu(\rho_l)(\rho_v - \rho). \quad (6)$$

### 3 Nucleation energy of bubbles

We deal here with bubbles which are small with respect to a typical size of the liquid phase. More precisely, a mass density field  $\rho$ , whose mean value is  $\rho_0$ , in a domain  $\mathcal{D}$  of volume  $v(\mathcal{D})$  represents a small bubble if  $\rho_l$  and  $\varepsilon \ll 1$  exist such that  $B = \{x \in \mathcal{D} \mid \left| \frac{\rho(x) - \rho_l}{\rho_0} \right| > \varepsilon\}$  satisfies  $\frac{v(B)}{v(\mathcal{D})} < \varepsilon$ . We note that, as  $\int_{\mathcal{D}} (\rho - \rho_0) dV = 0$ ,  $\left| \frac{\rho_0 - \rho_l}{\rho_0} \right| = O(\varepsilon)$ . We now evaluate (in the absence of capillarity effects and at the first order of approximation in  $\varepsilon$ ) the difference between the free energy of such a small bubble configuration and the homogeneous configuration of density  $\rho_0$ . This difference, which is part of the nucleation energy of the bubble, is  $w = \int_{\mathcal{D}} (\psi(\rho) - \psi(\rho_0)) dV$ .

As  $\int_{\mathcal{D}} \rho_0 dV = \int_{\mathcal{D}} \rho dV$ , the energy  $w = \int_{\mathcal{D}} [\psi(\rho) - a\rho - \psi(\rho_0) + a\rho_0] dV$  does not depend on the choice of the constant  $a$ . The total energy is well defined but its localization is somewhat arbitrary. This indetermination is related to the arbitrariness in the choice of chemical potentials. With the choice  $a = \mu(\rho_l)$  the energy is localized inside  $B$ . Indeed, with using the previous estimation for  $\rho_0 - \rho_l$  we obtain:

$$w = \int_B [\psi(\rho) - \mu(\rho_l)(\rho - \rho_l) - \psi(\rho_l)] dV + O(\varepsilon^2).$$

To the non-capillary part of nucleation energy of a bubble in an unbounded domain we have to add the interfacial (capillary) energy. In the Gibbs-Laplace theory we have for bubbles of radius  $R$  and surface tension  $\sigma$ :

$$W = 4\pi R^2 \sigma + \frac{4}{3}\pi R^3 [\psi(\rho_v) - \psi(\rho_l) + \mu(\rho_l)(\rho_l - \rho_v)]. \quad (7)$$

In the theory of second gradient fluids, following Cahn and Hilliard, we have:

$$W = \int_{\mathcal{D}} [\psi(\rho) - \psi(\rho_l) - \mu(\rho_l)(\rho - \rho_l) + \frac{C}{2}(\text{grad } \rho)^2] dV. \quad (8)$$

Let  $\mathcal{P} = \rho\mu - \psi$  denote the thermodynamic pressure. The conditions

$$\mu(\rho_l) = \mu(\rho_v), \quad (9)$$

$$\mathcal{P}(\rho_l) - \mathcal{P}(\rho_v) = -\frac{2\sigma}{R}, \quad (10)$$

valid - for isothermal equilibrium - only in Laplace theory, transform Eq.(7) into:

$$W = \frac{4}{3} \pi R^2 \sigma, \quad (11)$$

and imply that the nucleation energy of the bubble is the third of the creation energy of its interface. We can extend this result to the theory of second gradient fluids. Let  $\phi(\rho) = \psi(\rho) - \psi(\rho_l) - \mu(\rho_l)(\rho - \rho_l)$ ; by multiplying Eq. (6) by  $r^2$  and integrating it over  $[0, \infty]$  we get:

$$\int_0^\infty r^2 \left( \frac{C}{2} \rho'^2 - \phi(\rho) \right) dr + \int_0^\infty r^2 \left[ \phi(\rho_v) + \int_0^r \frac{2C}{x} \rho'^2(x) dx \right] dr = 0, \quad (12)$$

by integrating by parts and using Eq. (6) again, we obtain:

$$\int_0^\infty r^2 \left( \frac{C}{6} \rho'^2 + \phi(\rho) \right) dr + \left[ \frac{r^3}{3} \left( \phi(\rho) - \frac{C}{2} \rho'^2 \right) \right]_0^\infty = 0. \quad (13)$$

Because of (i) - (iii) of Sect. 2, the last term vanishes so that we obtain

$$W = 4\pi \int_0^\infty r^2 \left( \frac{C}{2} \rho'^2 + \phi(\rho) \right) dr = \frac{4}{3} \pi \int_0^\infty C r^2 \rho'^2 dr. \quad (14)$$

With denoting by  $R_m^2$  the mean value of  $r^2$  with respect to the measure  $\rho'^2 dr$ , Eq.(14) reads

$$W = \frac{4}{3} \pi R_m^2 \int_0^\infty C \rho'^2 dr. \quad (15)$$

For a large enough bubble (*i.e.* when  $\rho_l$  tends to  $\rho_l^P$ ):

(i)  $R_m$  is the radius,

(ii) Equation (15) reduces to Equation (11), as surface tension for plane interface is  $\int_0^\infty C \rho'^2 dr$ .

#### 4 Comparison between Laplace and second gradient theories. Equivalent bubbles

In second gradient theory the stress tensor in the center of a spherical bubble takes the value  $\tau = -p_v Id$  where  $p_v = \mathcal{P}(\rho_v)$ . As Equation (4) implies  $C \rho_v \Delta \rho_v = \rho_v (\mu(\rho_v) - \mu(\rho_l))$ , we have

$$p_v - p_l = \psi(\rho_l) - \psi(\rho_v) + \mu(\rho_l)(\rho_v - \rho_l). \quad (16)$$

Let us note that this difference is not equal to the corresponding difference of thermodynamic pressures as, for microscopic bubbles,  $\mu(\rho_l)$  differs from

$\mu(\rho_v)$ . As experimental results (Fisher, 1980) deal with measures of stresses, then we have to use  $p_v - p_l$  instead of  $\mathcal{P}(\rho_v) - \mathcal{P}(\rho_l)$  in the comparison between Laplace and second gradient theories. We can now define the surface tension and the radius of a bubble by identifying the nucleation energies and the pressure differences computed in both theories. Indeed  $p_v - p_l = \frac{2\sigma}{R}$  and  $\frac{4}{3}\pi \int_0^\infty Cr^2 \rho'^2 dr = \frac{4}{3}\pi R^2 \sigma$  imply

$$R = \left[ 2C \int_0^\infty r^2 \rho'^2 dr \right]^{\frac{1}{3}} [\psi(\rho_l) - \psi(\rho_v) + \mu(\rho_l)(\rho_v - \rho_l)]^{-\frac{1}{3}}, \quad (17)$$

and

$$\sigma = \left[ \frac{C}{4} \int_0^\infty r^2 \rho'^2 dr \right]^{\frac{1}{3}} [\psi(\rho_l) - \psi(\rho_v) + \mu(\rho_l)(\rho_v - \rho_l)]^{\frac{2}{3}}. \quad (18)$$

## 5 Conclusion

Let us notice that our treatment is based on Eq. (1) obtained by a continuum model. However, van Kampen (1964) obtained the same differential equation by using ideas and methods of statistical mechanics. Eq. (14) has allowed us to evaluate the nucleation free energy of a bubble, once the mass density profile is known, *i.e.* once the liquid phase density  $\rho_l$  has been assigned. Equation (16) allows us to understand the difference between thermodynamic and stress pressure. These two equations do not depend on a particular constitutive law and determine the radius and surface tension for a microscopic bubble. This is done by identifying the pressure jump and nucleation energy of Laplace theory with the corresponding quantities in the second gradient theory. This method has never been used in literature: for example, Cahn (1959) and Evans (1979) used for surface tension the expression valid for plane interfaces, and did not investigate the relationship between surface tension and radius. Our Eqs. (17)-(18) give such a relationship in an implicit form: in fact, both surface tension and radius depend on the density profile, which, in turn, depends on  $\rho_l$ . When the radius tends to infinity, our expression for surface tension reduces to that for plane interfaces. We observe that the relationship between  $\sigma$  and  $R$  depends on thermodynamic potential. Numerical calculations were performed by Dell'Isola, Gouin and Rotoli (1996) using equations (17)-(18) and van der Waals-type potential proposed by van Kampen (1964), Rocard (1967) and Peng (1976). It was able to observe that, for bubbles whose radius is close to the critical one, the predicted variations of the surface tension (for water and cyclohexane at 20°C) are in good agreement with the experimental observations (Katz *et al* 1976; Fisher & Israelachvili, 1980). This is not the case for the theoretical treatment proposed by Tolman (1947) and Kumar *et al* (1991).

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### **Abridged French version**

## **Rayon et tension superficielle des bulles microscopiques en théorie du second gradient**

### **Résumé**

La théorie de Laplace est inadaptée pour étudier les bulles de dimensions moléculaires. La théorie des fluides doués de capillarité interne nous permet de proposer une expression de la tension superficielle et du rayon des bulles comme fonctionnelles du potentiel chimique. Cette expression, en accord avec l'expérience, améliore les résultats obtenus par Cahn-Hilliard et Tolman.

### **Version française abrégée**

Pour étudier le comportement d'un fluide fortement hétérogène on ajoute à l'expression de la densité d'énergie libre d'un fluide homogène un terme limité, le plus souvent, à un développement au second ordre en gradients (Cahn, 1959; Serrin, 1986). Les équations du mouvement de ces fluides sont obtenues par la théorie du second gradient (Casal, 1961, Germain, 1973).

Tolman (1948) a étudié la tension superficielle des bulles en fonction de leur rayon. Des mesures expérimentales ont été faites pour des bulles de dimensions quasi moléculaires (Fisher, 1950; Kumar 1991). Pour de telles dimensions la théorie de Laplace est disqualifiée car la bulle de vapeur devient l'interface elle-même. Il est néanmoins important de donner une dimension et une énergie pour les germes microscopiques puis de les comparer à un modèle équivalent de type Laplace. On peut ainsi interpréter les résultats des expériences. Le modèle le plus simple de fluide du second gradient ne fait intervenir qu'une seule constante physique supplémentaire  $C$ . L'équation de l'équilibre est alors l'équation (1) (Serrin, 1986) où  $\tau$  s'interprète comme le tenseur des contraintes,  $\Omega$ ,  $\rho$  et  $P$  désignent respectivement le potentiel des forces de masse, la densité de masse et la pression hydrodynamique. Si les forces de masse sont négligeables, l'équilibre isotherme d'une bulle supposée sphérique dans une phase liquide de densité  $\rho_l$  est représenté par une solution de l'équation (4). Pour chaque valeur  $\rho_l$  dans une plage convenable on obtient un profil croissant unique et une valeur de la densité  $\rho_v$  au centre de la bulle. La règle de Gibbs est donc bien vérifiée. Nous comparons l'énergie libre d'un fluide homogène de densité  $\rho_o$  contenu dans un domaine  $D$  et l'énergie libre de la même masse de fluide dans  $D$  formée par un liquide homogène contenant une petite bulle  $V$ . Cela nous conduit aux expressions (7) et (8) pour l'énergie de nucléation  $W$  d'une bulle dans un do-



maine infini, respectivement en théorie de Laplace et en théorie du second gradient. Les conditions d'équilibre liquide-vapeur en théorie de Laplace permettent d'écrire  $W$  sous la forme de l'équation (11). La série d'égalités (5), (6), (12), (13), (14) montre que ce résultat se généralise sous la forme de l'équation (15) où  $R_m^2$  désigne la valeur moyenne de  $r^2$  relativement à la mesure  $\rho'^2$ . En théorie du second gradient, le tenseur des contraintes est sphérique à l'origine ainsi qu'à l'infini mais, alors qu'à l'infini la pression se confond avec la pression thermodynamique  $p_l = P(\rho_l)$ , cela est faux à l'origine où  $p_v = P(\rho_v) - C\rho_v \Delta\rho_v$ . En identifiant la différence de pression entre l'origine et l'infini ainsi que l'énergie de nucléation dans les deux théories, on obtient les définitions (17) et (18) pour le rayon  $R$  et la tension superficielle  $\sigma$  de la bulle. Notre raisonnement est basé sur l'équation (1) obtenue par un modèle de mécanique des milieux continus. Il faut noter que van Kampen (1964) a obtenu la même équation par des considérations de mécanique statistique. L'équation (14) nous permet d'évaluer l'énergie de nucléation à partir du profil de densité donc de  $\rho_l$ . La détermination du rayon et de la tension de surface d'une bulle microscopique par identification de l'énergie de nucléation et du saut de pression donné par la théorie de Laplace avec les quantités correspondantes en théorie du second gradient n'a jamais été utilisée dans la littérature: par exemple Cahn (1959) et Evans (1979) ont utilisé une expression de la tension superficielle valable pour une interface plane uniquement et n'ont pas étudié la relation liant le rayon et la tension superficielle. Les équations (17) et (18) permettent d'obtenir une telle relation sous forme implicite: le rayon et la tension superficielle dépendent tous deux du profil de densité qui lui-même dépend de  $\rho_l$ . Notre expression de la tension de surface se réduit, quand le rayon de la bulle  $R$  tend vers l'infini (*i.e.* quand  $\rho_l$  tend vers la valeur  $\rho_l^P$  valable pour une interface plane), à l'expression usuelle (Cahn, 1959). L'étude des variations de la tension superficielle en fonction du rayon nécessite le choix d'une loi d'état. Dell'Isola, Gouin et Rotoli (1996) ont utilisé les potentiels chimiques du type de van der Waals proposés par van Kampen (1964), Rocard (1967) ou Peng (1976), pour effectuer des calculs numériques: ils montrent que, pour des bulles de rayon voisin du rayon critique, la variation prévue de la tension superficielle correspond aux mesures expérimentales de Katz (1976) et Fisher (1980) alors que les prévisions de Tolman (1947) et Kumar (1991) ne sont pas réalisées.